

Quasi-one-dimensional spin dynamics in LiV_2O_4 : one-to-three dimensional crossover as a possible origin of heavy fermion state

Ryosuke Kadono,¹ Akihiro Koda,¹ Wataru Higemoto,² Kazuki Ohishi,³

Hiroaki Ueda,⁴ Chiharu Urano,^{5,*} Shin-ichiro Kondo,^{5,†} Minoru Nohara,⁶ and Hidenori Takagi⁵

¹*Muon Science Laboratory and Condensed Matter Research Center, Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), Tsukuba, Ibaraki 305-0801, Japan*

²*Advanced Science Research Center, Japan Atomic Energy Agency, Tokai, Naka, Ibaraki 319-1195, Japan*

³*Research Center for Neutron Science and Technology,*

Comprehensive Research Organization for Science and Society, Tokai, Naka, Ibaraki 319-1106, Japan

⁴*Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 605-8062, Japan*

⁵*Department of Advanced Materials Science, School of Frontier Sciences, University of Tokyo, Kashiwa, Chiba 277-8561, Japan*

⁶*Department of Physics, Okayama University, Okayama 700-8530, Japan*

Spin fluctuation in LiV_2O_4 is revisited by examining the earlier result of muon spin rotation/relaxation measurements. Instead of a relationship for the localized electron limit, one for *itinerant* electron systems between muon depolarization rate and spin fluctuation rate (ν_D) is employed to re-analyze data, which reveals that ν_D varies linearly with temperature ($\nu_D \propto T$) over a range 10^8 – 10^{12} s^{−1} for $0.02 \leq T < 10^2$ K. Such a linear- T behavior as well as the magnitude of ν_D is fully consistent with that of the magnetic relaxation rate previously observed by inelastic neutron scattering (INS), demonstrating that μSR and INS have a common time window over the fluctuation spectrum. The linear- T dependence of ν_D is understood as a specific feature predicted by a Hubbard model for intersecting one-dimensional (1D) chains. This quasi-1D character, which is co-existent with enhanced uniform susceptibility at low temperatures, supports the scenario of 1D-to-3D crossover for the microscopic origin of heavy-fermion behavior in LiV_2O_4 .

PACS numbers: 71.27.+a, 71.28.+d, 76.75.+i

Heavy fermion (HF) behavior observed in a cubic vanadium spinel, LiV_2O_4 , has been in the spotlight of broad interest,^{1,2} since it comprises one of remarkable examples in which only d -orbital electrons are relevant to the phenomenon. The formation of heavy quasiparticle (QP) state below a characteristic temperature, $T^* \simeq 20$ K, is suggested by large Sommerfeld coefficient ($\gamma \simeq 420$ mJ/molK²) and other bulk properties that are strikingly similar to typical f -electron HF compounds. Moreover, it has been inferred from the recent photoemission spectroscopy that a peak of the density of states (DOS) just above the Fermi energy (E_F) develops for $T < T^*$, which may correspond to the QP peak typically found for the f -electron systems.³

While these observations seem to favor the Kondo mechanism established for the f -electron compounds as a common microscopic origin for the HF behavior in LiV_2O_4 , approaches to support this scenario have been elusive. Earlier theoretical attempt to project the d -electron states (1.5 per $\text{V}^{3.5+}$ ion) onto the Kondo model by splitting them into two sub-bands by electronic correlation had to introduce unusually large Kondo coupling ($J_K \sim 10^3$ K) to overcome competing effect of the Hund coupling.^{4,5} Our μSR study on single-crystalline sample provided evidence against the formation of a spin-singlet state, as it showed presence of staggered vanadium moments at low temperatures far below T^* that was interpreted as the Kondo temperature (T_K) in this scenario.^{6,7} In the meantime, the importance of highly symmetric crystal structure and potential influence of geometrical

frustration has been stressed by various authors, leading to a large variety of theoretical models.^{8–17}

In the previous study using muon spin rotation and relaxation (μSR), we have shown on a powder specimen of LiV_2O_4 that the observed μSR signal consists of two components characterized by different response of depolarization rate (λ) to external magnetic field (H_0).⁶ In particular, the signal with λ showing least dependence on H_0 (λ_D , with a fractional yield $f \simeq 0.4$) is mostly independent of temperature below $\sim 10^2$ K, from which we suggested that the corresponding fluctuation rate derived from a general relation between λ and ν ,

$$\lambda \simeq \frac{2\delta_\mu^2 \nu}{\nu^2 + \gamma_\mu^2 H_0^2}, \quad (1)$$

is also independent of temperature ($\nu_D > 10^9$ s^{−1}). In contrast, λ associated with another signal (λ_S , with $1 - f \simeq 0.6$) is readily suppressed by H_0 , which has been ascribed to slowly fluctuating local magnetic moments ($\nu_S \sim 10^6$ – 10^7 s^{−1}). Although the occurrence of such a phase separation has been confirmed by subsequent μSR study on high-quality single-crystalline samples, the increased yield f ($\simeq 0.8$) strongly suggests that clarifying the origin of ν_D is essential to the understanding of electronic state in LiV_2O_4 .⁷

Despite the fact that LiV_2O_4 is metallic, the use of Eq. (1), which is valid in the limit of localized spins with ν determined by the local exchange interaction ($J \sim h\nu$), is presumed to be justified by the presence of staggered vanadium moments suggested by broad μSR linewidth

at low temperatures (which is also in line with presumption of the Kondo scenario for $T > T^*$).⁶ Besides this, Eq. (1) may be regarded as a good approximation at high temperatures where the electronic state is subject to strong damping by phonons. However, our recent μ SR study on another d -electron heavy fermion metal, $Y_{1-x}Sc_xMn_2$, has demonstrated that more precaution should be taken for the interpretation of depolarization at lower temperatures.¹⁸

Here, we revisit the spin dynamics of LiV_2O_4 on alternative basis that the staggered magnetic moments are carried by itinerant d electrons. The corresponding muon spin depolarization is described by a modified version of Eq. (1),

$$\lambda \simeq \frac{2\delta_\mu^2\nu}{\nu^2 + \gamma_\mu^2 H_0^2} \cdot \frac{\chi k_B T}{N_A \mu_B^2}, \quad (2)$$

where the factors additional to Eq. (1) stems from electronic density of state at the Fermi level with χ being the magnetic susceptibility, N_A the Avogadro number, and μ_B the Bohr magneton.^{19,20} As a consequence, our reanalysis indicates that ν_D is linearly dependent on temperature ($\nu \propto T$) with frequency ranging from 10^8 – 10^{12} s⁻¹, which accidentally serves to cancel the T -dependence of λ . The distilled behavior of ν_D turns out to be in excellent agreement with the previous result of inelastic neutron scattering (INS),²¹ strongly suggesting that both μ SR and INS have been observing a common phenomenon. Moreover, the linear- T dependence of spin fluctuation, which is commonly observed in $Y_{1-x}Sc_xMn_2$, is understood as a property characteristic to the spin-spin correlation of the intersecting Hubbard chains that simulate the pyrochlore lattice.²² This implies the crucial role of t_{2g} orbitals as one-dimensional (1D) chains that are under a strong geometrical constraint of pyrochlore lattice structure, and further suggests the dimensional crossover due to coupling between these chains as the primary origin of the heavy-fermion state.¹³

Since the previous study on single-crystalline sample indicates that muon depolarization is dominated by a component showing fast fluctuation (ν_D), we focus on the behavior of ν_D . The evaluation of ν_D using Eq. (2) requires additional information on magnetic susceptibility (χ) shown in Fig. 1, which has been obtained on the powder sample used for the previous μ SR measurement.⁶ Considering the behavior of χ observed in single-crystalline sample,^{2,23} we attribute the divergent behavior with $T \rightarrow 0$ to unknown paramagnetic impurities and decompose data into two parts,

$$\begin{aligned} \chi &= \chi_V + \chi_{\text{imp}} \\ &= \frac{a}{T + \theta} + \frac{b}{T}, \end{aligned} \quad (3)$$

where θ is the Weiss temperature. Curve fits using Eq. (3) yields $a = 0.387(5)$ emu·K/mol, $\theta = 74(2)$ K, and $b = 0.0131(2)$ emu·K/mol, in which the behavior of χ_V

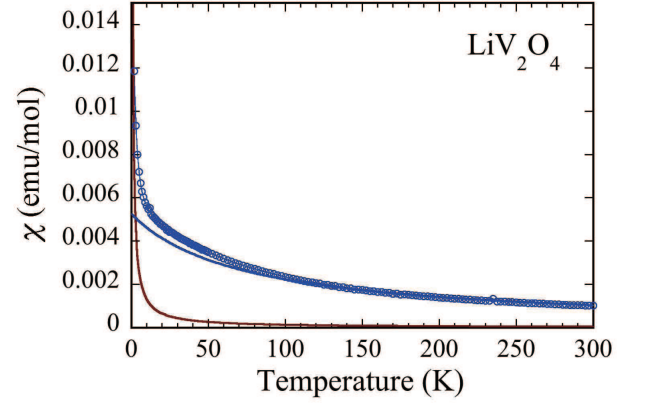


FIG. 1: (Color online) Magnetic susceptibility (χ) as a function of temperature in the powder specimen used for μ SR measurement in Ref.6. Solid curve shows the best fit using a form described in the text.

is in good agreement with that of single crystals. Henceforth we use $\chi = \chi_V$ for the input of Eq. (2). Assuming that the Curie term comes from free $V^{3.5+}$ spins ($1.5\mu_B$), the fractional yield of impurity phase estimated by b/T is 1.6% of the total volume. This is far smaller than that of primary μ SR signals (either f or $1 - f$ with $f \simeq 0.4$), indicating that the paramagnetism of the impurity phase is irrelevant to the interpretation of μ SR data.

Another important quantity in Eq. (2) is the hyperfine parameter, δ_μ . The muon Knight shift measurements in both powder and single-crystalline samples yield $\delta_{\mu(D)} \simeq 0.5 \pm 0.2$ GHz/ μ_B that corresponds to the signal with ν_D .^{6,7} Apart from the large error due to broad linewidth, it is in good agreement with calculated value, $\delta_{\mu(D)} = 0.143$ GHz/ μ_B , for muons that occupy a site in the center of cyclic vanadium hexamer (as inferred from the observed μ SR linewidth due to nuclear magnetic moments at high temperatures) and are subject to the magnetic dipolar fields from vanadium ions.⁶ Since the experimental value of hyperfine parameter has large uncertainty due to broad linewidth, we use the calculated value for the evaluation of ν_D below.

Fig. 2 shows muon depolarization rate (λ_D) under zero external field, deduced by curve fits using a sum of two exponential damping,⁶

$$P_z(t) = f \exp(-\lambda_D t) + (1 - f) \exp(-\lambda_S t).$$

Although the data are scarce particularly at higher temperatures, λ_D is only weakly dependent on temperature with a tendency of gradual increase with decreasing temperature, which is qualitatively similar to the behavior of χ_V (see the inset of Fig. 2). These features are remarkably similar to that observed in $Y_{1-x}Sc_xMn_2$ with greater Sc content ($x \geq 0.07$).¹⁸

The evaluation of ν_D from λ_D is straightforward by

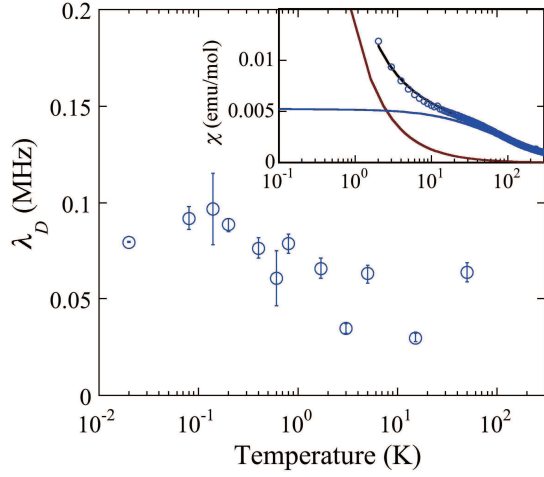


FIG. 2: (Color online) Muon depolarization rate in LiV_2O_4 reproduced using data published in Ref.6 for the component showing fast fluctuation (ν_D). Inset: reproduction of Fig. 1 with logarithmic scale for temperature.

using Eq. (2) in a modified form,

$$\nu_D \simeq \frac{2\delta_\mu^2}{\lambda_D} \cdot \frac{\chi k_B T}{N_A \mu_B^2}, \quad (4)$$

where $H_0 = 0$ for the present condition of zero external field. The result is plotted in Fig. 3 together with data of INS,²¹ where one can observe that ν_D falls on a straight line representing linear relation to temperature ($\nu_D \propto T$) over a T range of three decades. This is again strikingly similar to the behavior of spin fluctuation rate observed in $\text{Y}_{1-x}\text{Sc}_x\text{Mn}_2$ with $x \geq 0.07$.¹⁸

According to a numerical simulation of quarter-filled Hubbard chains (or rings) by path integral quantum Monte Carlo method, the spin dynamics is predicted to exhibit a linearly T -dependent relaxation rate in the spin-spin correlation,

$$\nu(\mathbf{q}) = \nu_0 + c(\mathbf{q}) \cdot T, \quad (5)$$

where ν_0 comes from residual ferromagnetic spin correlation (corresponding wave vector $\mathbf{q} = 0$).²² It is also inferred from the simulation that Eq. (5) depends only weakly on \mathbf{q} and other parameters such as U/t (where U and t are the on-site Coulomb energy and the transfer integral between nearest neighboring vanadium sites in the Hubbard model, respectively). The observed behavior of ν_D is perfectly in line with the above prediction with $\nu_0 \simeq 0$. As shown in Fig. 3, the magnitude of ν_D as well as its linear- T dependence is in excellent agreement with the spin relaxation rate observed in INS at $q = Q_c = 0.64 \text{ \AA}^{-1}$ (around which a broad peak is observed below T^*) after subtracting the residual term, $\Gamma_q(T \rightarrow 0) \equiv \Gamma_0 \simeq 1.5 \text{ meV}$.²¹ The difference between ν_0 (μSR) and Γ_0 (INS) may be attributed to that in the sensitive q range of observation, as the q -integrated Γ_q

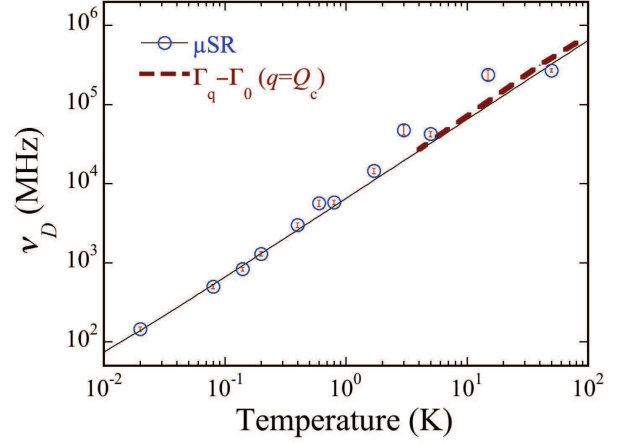


FIG. 3: (Color online) Spin fluctuation rate (ν) as a function of temperature in LiV_2O_4 . Thin solid line shows linear T dependence ($\nu \propto T$). Inelastic neutron scattering (INS) data are quoted for comparison, where the dashed curve shows the linewidth $(\Gamma_q - \Gamma_0)/h$ at $Q_c = 0.64 \text{ \AA}^{-1}$ with $\Gamma_0 \simeq 1.5 \text{ meV}$.²¹ (See text for more detail.)

(for $0.6 < q < 1.3 \text{ \AA}^{-1}$) shows tendency of smaller Γ_0 .²¹ It must be remembered, however, that ν_D is subject to certain ambiguity due to the broadness of linewidth $\delta_{\mu(D)}$ observed in the muon Knight shift measurement.

While the comparison between ν_D and Γ_q demonstrates that both μSR and INS probe nearly identical part of the spin fluctuation spectrum in LiV_2O_4 , it also confirms that ^7Li -NMR has a completely different time window of observation.^{1,24-28} Considering estimated hyperfine field on ^7Li nuclei ($A_{\text{hf}} \simeq 0.258 \text{ T}/\mu_B$ in Ref.25, or $0.171 \text{ T}/\mu_B$ in Ref.26), the corresponding parameter δ_μ in Eq. (4) is evaluated to be $\gamma_{\text{Li}} A_{\text{hf}} \simeq 17.8\text{-}26.9 \text{ MHz}/\mu_B$ (where $\gamma_{\text{Li}} = 2\pi \times 16.546 \text{ MHz/T}$). Since the spin-lattice relaxation rate ($1/T_1 = \lambda$) is reported to vary over a range of $10^0\text{-}10^2 \text{ s}^{-1}$ and to follow the Korringa relation ($\lambda/T \sim 2.0\text{-}2.25 \text{ s}^{-1}\text{K}^{-1}$) for $T < T^* \simeq 20 \text{ K}$,^{1,24-26} the corresponding spin fluctuation rate evaluated by Eq. (4) levels off to take a constant value, $\nu_{\text{Li}} \sim 10^{13} \text{ s}^{-1}$ ($T \ll T^*$). Interestingly, the estimation of ν_{Li} using relationship between the electronic specific heat coefficient and $N(E_F)$, $\gamma = (2\pi^2/3)k_B^2 N(E_F)N_A = 0.420 \text{ J/mol K}^2$ yields

$$\nu_{\text{Li}} \simeq \frac{1}{\hbar N(E_F)} = \frac{2\pi^2 k_B^2 N_A}{3\hbar \gamma} = 1.7 \times 10^{13} \text{ s}^{-1}. \quad (6)$$

This is in excellent agreement with the experimental observation, and strongly suggests that $1/T_1$ in ^7Li -NMR is dominated by the Pauli paramagnetism. It should be stressed that the above frequency is beyond the limit of observation for μSR under the present condition, because the corresponding λ would be less than 10^{-2} MHz .

A theoretical model by Fujimoto presumes the quasi-1D character of the t_{2g} bands associated with the pyrochlore lattice (consisting of intersecting chains of t_{2g}

orbitals) as an essential basis for the description of electronic state in LiV_2O_4 , because the hybridization between the 1D bands will be strongly suppressed owing to the geometrical configuration.¹³ It is interesting to note that such quasi-1D bands may have singularities in DOS, as in an analogous case of A15-type intermetallic compounds (e.g., V_3Si) where it is predicted that $N(E) \propto 1/(E - E_c)^{1/2}$ with E_c being the position of the d band.²⁹ The model incorporates the hybridization as a perturbation to the 1D Hubbard bands, which yields an energy scale (T^*) that characterizes the dimensional crossover from 1D to 3D as the Fermi-liquid state develops with decreasing temperature below T^* . The calculated γ taking account of the latter as the leading correction to the self-energy yields a large value, consistent with the experimentally observed ones. The progression of hybridization also induces the enhancement of the 3D-like spin correlation that would appear as the enhancement of uniform susceptibility, while the spin fluctuation is dominated by the staggered component of 1D Hubbard chains. The increase in χ ($= \chi_V$) with decreasing temperature shown in Fig. 1 is understood as the manifestation of such a dimensional crossover, as it perfectly follows the prediction by the relevant theory.¹³ The quasi-1D character of the low-energy spin fluctuation preserved below T^* coexisting with the enhanced χ , which is commonly observed in $\text{Y}_{1-x}\text{Sc}_x\text{Mn}_2$, comprises strong evidence of such a scenario.

It would be honest to mention that the muon depolarization rate (λ , from which ν is deduced) does not provide any criterion in itself to decide the credibility of the present interpretation based on itinerant model compared with that based on the local spin model adopted in our previous report. However, the itinerant model has substantial merit as it provides a coherent understanding of spin fluctuation in metallic LiV_2O_4 without resorting

to the splitting of t_{2g} band for a part of vanadium ions to bear “local” spins, where such a band splitting is yet to be demonstrated experimentally.

Finally, we briefly mention the signal component with slower spin fluctuation observed by μSR .^{6,7} This component is characterized by relatively small hyperfine parameter ($\delta_{\mu(S)} = 23\text{--}34 \text{ MHz}/\mu_B$), from which fluctuation rate ν_S is evaluated by Eq. (4) to yield $10^6\text{--}10^7 \text{ s}^{-1}$ at low temperatures ($T < 1 \text{ K}$). Considering the fact that the fractional yield of this component decreases drastically in the single-crystalline samples ($1 - f \simeq 0.2$), one may be inclined to associate this component to some unknown impurity phase. However, there is no other experimental evidence for such a second phase having different chemical form with the relative yield as high as $\sim 20\%$. Thus more careful investigation would be needed to clarify the origin of this slow fluctuation.

In conclusion, we have shown that reanalysis of muon depolarization rate in LiV_2O_4 using the model of spin depolarization for the itinerant electron systems yields spin fluctuation rate that is linearly dependent on temperature. This result turns out to be fully consistent with that of the previous inelastic neutron scattering experiment, providing a coherent understanding of the spin dynamics by the theoretical model of intersecting 1D-Hubbard chains that simulates pyrochlore lattice. The persistent quasi-1D spin dynamics coexists with the enhanced uniform susceptibility at lower temperature ($T < T^*$), which is common to another d -electron heavy-fermion system $\text{Y}_{1-x}\text{Sc}_x\text{Mn}_2$. These observations strongly suggest that geometrically constrained t_{2g} band is the primary stage for the formation of heavy quasiparticles with the 1D-to-3D dimensional crossover as a possible mechanism of effective mass enhancement.

* Present address: National Institute of Advanced Industrial Science and Technology, Tsukuba 305-8561, Japan

† Present address: Materials Laboratories, SONY Corporation, Tokyo 108-0075, Japan

¹ S. Kondo, D. C. Johnston, C. A. Swenson, F. Borsa, A. V. Mahajan, L. L. Miller, T. Gu, A. I. Goldman, M. B. Maple, D. A. Gajewski, E. J. Freeman, N. R. Dilley, R. P. Dickey, J. Merrin, K. Kojima, G. M. Luke, Y. J. Uemura, O. Chmaissem, and J. D. Jorgensen, Phys. Rev. Lett. **78**, 3729 (1997).

² C. Urano, M. Nohara, S. Kondo, F. Sakai, H. Takagi, T. Shiraki, and T. Okubo, Phys. Rev. Lett. **85**, 1052 (2000).

³ A. Shimoyamada, S. Tsuda, K. Ishizaka, T. Kiss, T. Shimojima, T. Togashi, S. Watanabe, C. Q. Zhang, C. T. Chen, Y. Matsushita, H. Ueda, Y. Ueda, and S. Shin, Phys. Rev. Lett. **96**, 026403 (2006).

⁴ V. I. Anisimov, M. A. Korotin, M. Zöhl, T. Pruschke, K. Le Hur, and T. M. Rice, Phys. Rev. Lett. **83**, 364 (1999).

⁵ H. Kusunose, S. Yotsuhashi, and K. Miyake, Phys. Rev. B **62** 4403 (2000).

⁶ A. Koda, R. Kadono, W. Higemoto, K. Ohishi, H. Ueda, C. Urano, S. Kondo, M. Nohara, and H. Takagi, Phys. Rev. B **69**, 012402 (2004).

⁷ A. Koda, R. Kadono, K. Ohishi, S. R. Saha, W. Higemoto, Y. Matsushita and Y. Ueda, J. Phys.: Condens. Matter **17**, L257 (2005).

⁸ C. Lacroix, Can. J. Phys. **79**, 1469 (2001).

⁹ P. Fulde, A. N. Yaresko, A. A. Zvyagin, and Y. Grin, Europhys. Lett. **54**, 779 (2001).

¹⁰ N. Shannon, Eur. Phys. J. B **27**, 527 (2002).

¹¹ S. Burdion, D. R. Grempel, and A. Georges, Phys. Rev. B **66**, 045111 (2002).

¹² J. Hopkinson and P. Coleman, Phys. Rev. Lett. **89**, 267201 (2002).

¹³ S. Fujimoto, Phys. Rev. B **65**, 155108 (2002).

¹⁴ H. Tsunetsugu, J. Phys. Soc. Jpn. **71**, 1844 (2002).

¹⁵ Y. Yamashita and K. Ueda, Phys. Rev. B **67**, 195107 (2003).

¹⁶ M. S. Laad, L. Craco, and E. Muller-Hartmann, Phys. Rev. B **67**, 033105 (2003).

- ¹⁷ R. Arita, K. Held, A.V. Lukoyanov, and V. I. Anisimov, Phys. Rev. Lett. **98**, 166402 (2007).
- ¹⁸ M. Miyazaki, R. Kadono, M. Hiraishi, T. Masuda, A. Koda, K. M. Kojima, T. Yamazaki, Y. Tabata, and H. Nakamura, J. Phys. Soc. Jpn. in press (arXiv:1105.2360).
- ¹⁹ T. Moriya and A. Kawabata, J. Phys. Soc. Jpn. **34**, 639 (1973); *ibid.* **35**, 669 (1973).
- ²⁰ H. Hasegawa and T. Moriya, J. Phys. Soc. Jpn. **36**, 1542 (1974).
- ²¹ S.-H. Lee, Y. Qiu, C. Broholm, Y. Ueda, and J. J. Rush, Phys. Rev. Lett. **86**, 5554 (2001).
- ²² J. D. Lee, Phys. Rev. B **67**, 153108 (2003).
- ²³ Y. Matsushita, H. Ueda, and Y. Ueda, Nature Mater. **4**, 845 (2005).
- ²⁴ D. C. Johnston, S.-H. Baek, X. Zong, F. Borsa, J. Schmalian, and S. Kondo, Phys. Rev. Lett. **95**, 176408 (2005).
- ²⁵ A. V. Mahajan, R. Salo, E. Lee, F. Borsa, S. Kondo, and D.C. Johnston, Phys. Rev. B **57**, 8890 (1998).
- ²⁶ N. Fujiwara, H. Yasuoka, and Y. Ueda, Phys. Rev. B **59**, 6294 (1999).
- ²⁷ W. Trinkl, N. Büttgen, H. Kaps, A. Loidl, M. Klemm, and S. Horn, Phys. Rev. B **62**, 1793 (2000).
- ²⁸ H. Kaps, M. Brando, W. Trinkl, N. Büttgen, A. Loidl, E.-W. Scheidt, M. Klemm, and S. Horn, J. Phys.: Condens. Matter **13**, 8497 (2001).
- ²⁹ J. Labbé, Phys. Rev. **158**, 647 (1967).